

JAPANESE

[JP,06-157955,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD EXAMPLE CORRECTION OR
AMENDMENT

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to a water-based ink and the aquosity ink jet composition from which curl of the printed regular paper element is removed more in details.

[0002]

[Background of the Invention]Ink jet printing is the non-shock nature method which produces the ink droplet to which it adheres on paper or a base material like a bright film in response to an electronic digital signal. Heat or a bubble jet type drops ink jet printer on demand (drop-on-demand) is widely used as an output for personal computers of an office and a home. The water-based ink used for ink jet printing has water as the main ingredients. To the non-aqueous ink in which most comprises an organic solvent, water is nontoxic, is a non-inflammability and has the advantage of not being harmful to environment. Water is also the outstanding medium for distributed paints or dissolution colors again.

[0003]However, condensing and using a lot of water is accompanied by some disadvantages.

Compared with a low-boiling point organic solvent, a vapor rate is slow, and this reduces a drying rate, therefore water reduces printing speed. Water interacts with paper further and causes two main distortion known as the wrinkles of paper, and curl of paper. The wrinkles of paper are distortion which produces a shock, a hollow, and other non-** at random on printing paper, and makes wrinkles in the appearance of paper. Curl is a phenomenon which the edge of paper moves toward the center of

paper. The direction of curl may be a side which is a side on which paper was printed or is not printed (the latter is known as "reverse curl").

[0004]One day or two days may be taken for curl to appear immediately after a print or to appear. In the final state, a paper sheet takes the gestalt of a pipe. The paper which curled cannot be accumulated, or cannot be opened on a sheet, therefore a user causes extraordinary inconvenience. The sheet which curled cannot be used for the process which takes ***** like [it is difficult and] medium supply, tracking, and print consistency to extending or saving. Curl is the most common on a solid restoration print (solid fill printing), therefore is the most serious problem in a chart as what is contrasted with the print of this chapter. For the same reason, it is mainly the concerns in 4 color print with a remarkable chart. If a heating element (used since the drying rate of a water-based ink is generally gathered) is used, being urged to curl of paper is publicly known.

[0005]Various mechanical contrivance for reducing curl like a heat roller and a tension applicator has been tried. These devices are only effective in a peripheral area, and increase the cost and the size of a printer considerably (the heat roller used in order to reduce curl differs from the heater used since a drying rate is gathered.). In the case of the former heat roller, heat is applied to the both sides of paper after a print, but when it is the latter heater, heat is applied into a print process.

[0006]It is also publicly known by reforming a print medium to reduce curl. However, since consumers like overwhelmingly the printer which can use what cost starts and is sold to the wide range office paper, especially the electro photography copying machine paper commercial scene, or a what is called "regular paper" printer, this approach is not dramatically desirable. Therefore, the aqueous ink composition which can be printed on all the page charts is required for this industry, without producing paper curl, therefore it is less necessary for the inefficient and troublesome mechanical contrivance or the special print medium which cost requires.

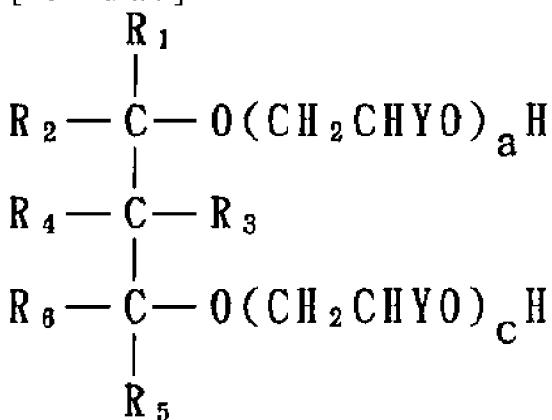
[0007]The above-mentioned necessity is satisfied more by low cost rather than obtained by correcting equipment and a medium, without being accompanied by any harmful operations like induction of the ink composition (kogation) of this invention, i.e., a Kogation, low printing quality, or preservation instability.

[0008]

[Summary of Invention]In a certain mode, this invention provides the aqueous ink composition containing at least one curl inhibitor of sufficient quantity to remove substantially curl of an aqueous carrier medium, colorant, and a regular paper printing element. Colorant is a pigment dispersion object or a color. a curl inhibitor has at least 4.5% of water solubility (4.5 g per 100 g of water) at 25 ** --

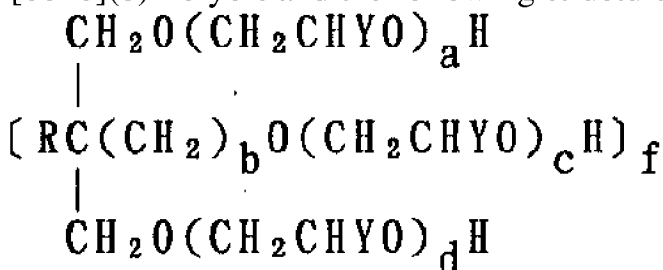
desirable -- : [0009](a) 1,3-diol, 1,3,5-triol, amino-1,3-diol, and the following structural formula :

[Formula 9]



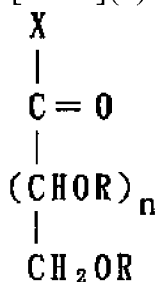
[Independently R^1 , R_2 , R_4 , R_5 , and R_6 among a formula H, Are C_nH_{2n+1} (it is $n=1-4$ here) or $C_nH_{2n}O$ (CH_2CHYO) $_bH$ (it is $n=1-6$ and $b=0-25$ here), and; $R_3=H$, C_nH_{2n+1} (it is $n=1-4$ here), $C_nH_{2n}O$ (CH_2CHYO) $_bH$ (it is $n=1-6$ and $b=0-25$ here), or $(CH_2)_eNXZ$ (here -- X and Z -- independently -- H -- it CH_3 (ing) and) Are C_2H_5 or $C_2H_4O(CH_2CHYO)_dH$ (it is $d=0-25$ and $e=0-3$ here), and; $Y=H$ or CH_3 ; a, and c independently. The polyoxyalkylene derivative which has that it is 0-25 and the totals of; and a CH_2CHYO unit are 0-100];

[0010](b) Polyols and the following structural formula : [Formula 10]



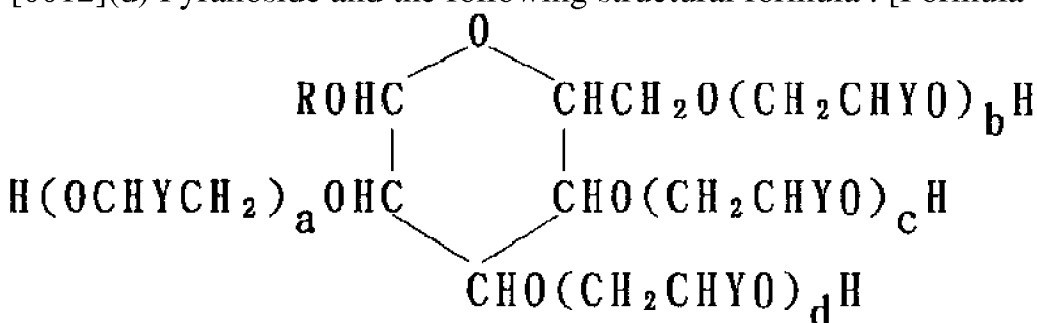
[Among a formula, independently, R is H, C_nH_{2n+1} (it is $n=0-4$ here), or $CH_2O(CH_2CHYO)_eH$, and; $Y=H$, CH_3 ; $b=0$, or 1; a, Although c, d, and e are 0-40 independently and the totals of; $f=1-6$; and a CH_2CHYO unit are 0-100, The polyoxyalkylene derivative which has that however, e is not 0 when it is a, b, c, $d=0$, and $f=1$ and R is not H but a, c, $d=0$, b, and $f=1$];

[0011](c) The following structural formula : [Formula 11]



[The inside of a formula, $X=H$, OH, $CH_2O(CH_2CHYO)_aH$, It is $O(CH_2CHYO)_bH$ or OM (OM is a metallic cation here), and is : $n=2-7$; $R=(CH_2CHYO)_c$ (here). Compound which has that $Y=H$ or CH_3 ; a, b, and c are 0-25 independently, and the totals of; and a CH_2CHYO unit are 0-125];

[0012](d) Pyranoside and the following structural formula : [Formula 12]



The polyalkoxy alkylene derivative which has [it is inside of a formula, $R=H$, or C_nH_{2n+1} (it is $n=0-4$

here), and; a, b, c, and d are 0-30 independently, and the totals of; Y=H or CH₃; and a CH₂CHYO unit are 0-120];

[0013](e) Structural-formula: H-(OCH₂ CHY)_xOH (inside of formula, Y=H or CH₃, and x= 3-20); and the (f) structural formula which are the following : Z₁Z₂N(CH₂CH₂NZ₃)_nZ₄ The inside of [type, Z₁, Z₂, Z₃, and Z₄ are _aH (here) independently (CH₂CHYO). It is chosen from the group which consists of a polyoxyalkylene derivative of the aliphatic polyamine which has that it is Y=H or CH₃; n=1-20; a is 0-20 independently, and the totals of; and a CH₂CHYO unit are 3-200].

[0014] In another mode, especially this invention is the method of reducing paper curl of the regular paper print elements which consist of a process of usually giving an ink composition to a base paper, A method containing at least one curl inhibitor of sufficient quantity for the above-mentioned ink composition to remove substantially paper curl of an aqueous carrier medium, colorant, and the above-mentioned base material is included.

[0015] Besides the advantage of removing curl, it was found out by the surprising thing that the ink of this invention is useful for a still more specific use. For example, it became clear that "paddling" can be controlled by the ink of a certain kind using the curl inhibitor written in this specification so that it might explain in more detail below. "Paddling" shows that ink spreads on a cover plate from a pen nozzle, and this has a possibility of producing a defect at the time of a print. Thereby, although it was also found out that the color system ink of this invention causes increase of chroma saturation and a color gamut, the range of dye concentration became large, it faced prescribing ink, and its flexibility increased further rather than the former was possible (refer to U.S. Pat. No. 5,118,350).

[0016] The person skilled in the art recognizes that many compounds enumerated above are the publicly known additive agents for the ink jet ink for other purposes. For example, U.S. Pat. No. 5,100,469 teaches that the drying rate of print ink jet ink may be improved by adding 0.1 thru/or about 8% of the weight of a ****- erythritol, a TORIMECHI roll alkyl compound, TORIMECHI roll alkylamine, or its salt. Similarly, JP,2-14262,A and JP,2-14260,A teach the quick-drying color system ink jet ink which has 0.5 to 25% of the weight of trimethylolethane, or trimethylolpropane, respectively combining 1.0 to 10% of the weight of lower alcohol.

[0017] A majority of such compounds are publicly known moisturizers. However, generally these compounds have been used by too low concentration for obtaining the curl prevention profits taught to this specification. Nevertheless, when these compounds were used by sufficient concentration to produce a curl prevention operation, it was found out that it is a still effective moisturizer.

[0018]

[A detailed description of an invention] The water-based ink of this invention is suitable for an ink jet printer and especially using it for a heat ink jet printer generally especially. This ink composition includes both paints and color system ink. Ink suits the requirements for a specific ink jet printer, and provides the sufficiently publicly known light stability which was able to take balance, dirt tolerance, viscosity, surface tension, optical density, low toxicity, high substance compatibility, and a drying rate in this industry.

[0019] An aqueous carrier medium aqueous carrier medium is a mixture of water or water, and at least one water soluble organic solvent other than a curl inhibitor. Generally deionized water is used. A water soluble organic solvent is publicly known enough, and the example of representation is indicated by U.S. Pat. No. 5,085,698 (this specification is joined by reference in the description content).

Selection of the suitable mixture of water and a water soluble organic solvent is based on the drying time of desirable surface tension and viscosity, selected colorant, and ink, and the requirements for the medium base material with which ink is printed. The mixture of the water soluble organic solvent (for example, diethylene glycol) and deionized water which have at least two hydroxyl groups is preferred as an aqueous carrier medium.

[0020]When using the mixture of water and an organic solvent as an aqueous carrier medium, water contains 60 % of the weight - 95% of the weight of an aqueous carrier medium preferably 30 % of the weight - 95% of the weight on the basis of the gross weight of an aqueous carrier medium including the weight of the curl inhibitor. The quantity (the weight of a curl inhibitor is included) of an aqueous carrier medium, When choosing an organic color, choosing an inorganic pigment about 84 to 99.8% preferably about 70 to 99.8% on the basis of the gross weight of ink and choosing about 70 to 99.8%, and a color preferably about 25 to 99.8%, it is 80 to 99.8% of range.

[0021]In colorant this invention, useful colorant is a pigment dispersion object and a color. The term of "paints" means the colorant used in the insoluble granular state. The term of a "color" means the colorant used in the state of fusibility. The term of a "pigment dispersion object" shows the mixture of paints and a dispersing agent so that it may be publicly known in this industry, and as it is used into this specification. Preferably, a dispersing agent is a polymers dispersing agent.

[0022]Color: As a useful color, negative ion nature, positive ion nature, both sexes, and a nonionic color are mentioned to this invention. Such a color is publicly known enough to a person skilled in the art. A negative ion nature color is a color which produces coloring negative ion in an aqueous solution, and a positive ion nature color produces a coloring positive ion in an aqueous solution. Generally, a negative ion nature color contains carboxylic acid or a sulfonic group as an ion portion. A positive ion nature color usually contains a quaternary nitrogen group. Both sexes colors are negative ion nature and positive ion nature, or have both electric charges as a function of solution pH. A certain kind of nonionic color has sufficient water solubility to use for a water-based ink. The color which has solubility insufficient in an aqueous carrier medium is processed as paints, and it may be distributed in order to use for a water-based ink by the same method as the following.

[0023]Generally the color of the above-mentioned complete range is classified according to the end use. Some of colors of the more useful kind of this invention are edible, distribution, mordanting, a bat, a solvent, and reactive dye acidity, basicity, and directly. These kinds of all colors One or the peculiar functional group beyond it, For example, a nitroso compound, a nitro compound, an azo compound, a stilbene compound, doria -- a reel methane compound, a xanthene compound, a quinoline compound, and a thiazole compound. An azine compound, an oxazine compound, a thiazine compound, an amino ketone compound, It has an anthraquinone compound, an indigoid compound and a phthalocyanine compound, a diphenylmethane compound, an acridine compound, a quinoline compound, methine or a poly methine compound, indamine, or the India phenyl compound, and these are all publicly known enough to a person skilled in the art. The color and quantity of a color which are used for an ink composition are one function of selection dramatically, and are based on the purity of the desirable color of the print attained mainly using ink, and a color, and its concentration. Sufficient vividness does not arise with a color being low concentration. The dark color which its high concentration cannot be [print head performance] insufficient, or it cannot permit is produced. 0.05 to 8 % of the weight of colors exist in 0.1 to 5% of the weight of quantity still more preferably preferably 0.01 to 20% of the weight on the basis of the gross weight of ink.

[0024]Paints: Paints useful to distribution are independent, or combine and contain wide range organicity and inorganic pigment. An insoluble color may also be indicated substantially [medium /

aqueous carrier] here. Paints particles need to be small enough for making into easy flow the ink in the projection nozzle which passes an ink jet printing device and which usually has a diameter of the range of 10-50 microns especially. Particle diameter affects the stability of a pigment dispersion object further. The Brownian motion of a fine grain is useful to prevent sedimentation of particles. When particle diameter is small, it is desirable also for maximum color concentration. The ranges of useful particle diameter are about 0.005 micron - 15 microns. The particle diameter of paints is 0.005-5 microns, and is 0.01-0.5 micron most preferably.

[0025]The selected paints can be used with desiccation or a humid gestalt. For example, paints are usually manufactured in an aqueous medium and the paints produced as a result are obtained as a water wettability filter press cake. In a filter press cake gestalt, paints are not condensed to a grade like [in the case of being a dry gestalt]. Therefore, the paints of a water wettability filter press cake gestalt do not need equivalent solution condensation in the process of manufacturing ink from dry paints. The typical commercial desiccation and filter press cake paints which it faces carrying out this invention and can be used are indicated by above-mentioned U.S. Pat. No. 5,085,698.

[0026]This invention may be carried out using the microscopic particles of metal or a metallic oxide. For example, metal and a metallic oxide fit preparation of magnetic ink jet ink. The oxide of detailed particle diameter, for example, silica, alumina, a titania, etc. may be chosen. Detailed grinding metal particles, for example, copper, iron, steel, aluminum, and an alloy can be chosen for a suitable use. In the case of an organic color, ink may contain paints to about 30 % of the weight, but generally 0.1 to 15% of the abbreviation of the weight of the total ink composition is about 0.1 to 8% preferably at most heat ink jet printing uses. Since ink tends to contain the paints of high weight % compared with the ink which used the organic color and an inorganic pigment generally has specific gravity higher than an organic color when choosing an inorganic pigment, it is height of about 75% in some cases.

[0027]Dispersing agent: A polymers dispersing agent is a desirable dispersing agent for paints. As a polymers dispersing agent suitable for operation of this invention, AB, BAB, or ABC block copolymer is mentioned. Since a polymers kind with the tendency which plugs up a pen nozzle is not included, the polymers dispersing agent manufactured by the basis transfer polymerizing method is the most preferred. Suitable AB or BAB block copolymer, and its composition are indicated by above-mentioned U.S. Pat. No. 5,085,698. Suitable ABC triblock copolymer and those composition are indicated by Ma et al., and USSN 07/838,181 (February 20, 1992 application) (this specification is joined by reference in the description content). Although a random copolymer can be used as a dispersing agent, they are not effective in stabilizing a pigment dispersion object like block polymer, therefore preferred.

[0028]Generally as for a polymers dispersing agent, 0.1 to 30 % of the weight of abbreviation of the total ink composition exists preferably in about 0.1 to 8% of the weight of the range. The dispersion stability of paints particles will be damaged if a polymers dispersing agent exists insufficiently. everything but a desirable polymers dispersing agent compound -- or a detergent compound may be instead used as a dispersing agent. As these examples, negative ion nature, positive ion nature, nonionic, or an ampholytic surface active agent is mentioned. Non-polymers and the detailed table of some polymers dispersing agents, McCutcheon's Functional. Materials and North American. It is shown in Edition, 1990 Manufacturing Confection Publishing Co., Glen Rock, NJ, and the paragraph (110-128 pages) about the dispersing agent of 07452 (the description content by reference.). This specification is joined.

[0029]A curl inhibitor suitable for using for curl inhibitor this invention contains the polyhydroxy

basis and/or polyoxyalkylene group which are obtained by the reaction of a polyhydroxy basis and alkylene oxide. This compound has at least 4.5% of water solubility (they are 4.5 copies of curl inhibitors in 100 copies of water), and is represented with 25 ** by the compound of the kind indicated below.

[0030](a) Those polyoxyalkylene derivatives that have 1,3 diol, 1,3,5-triol, amino-1,3-diol, or the above-mentioned structural formula constitute the curl inhibitor of the first kind suitable for using for this invention. As an example of the curl inhibitor contained in this kind, 2,2-dimethyl- 1,3-propanediol, 2-methyl-2-ethyl-1,3-propanediol, 2,2-diethyl- 1,3-propanediol, 2-methyl-2-propyl-1,3-propanediol, 1,2,4-butanetriol, The 3-methyl- 1 and 3, 5-pentanetriol, 1 and 3, 5-pentanetriol, 2,4-pentanediol, the 2-methyl- 2, 4-pentanediol, 1,1,1-tris(hydroxymethyl) aminomethane, 2,2-bis (hydroxymethyl)-2,2', and 2''-nitrilotriethanol, 2-amino-2-methyl-1,3-propanediol, and 2-amino-2-ethyl-1,3-propanediol are mentioned. Mineral acid like chloride may neutralize an amino compound all or in part. A polyoxyalkylene compound is derived from the compound of the above-mentioned list.

[0031](b) Another curl inhibitor of a kind suitable for using for this invention comprises the oxyalkylene derivative which has polyol and the above-mentioned structural formula. The term of "polyol" as used in this kind means the compound which has 3-8 hydroxyl groups which combine a hydroxyl group or a hydroxymethyl group with a main chain. The term of an "oxyalkylene derivative" means one which replaces hydrogen on a hydroxyl group, or the oxyalkylene repeating unit beyond it. As some examples of this kind of polyhydroxy compound, 2-hydroxymethyl-1,3-propanediol, A 2-ethyl-2-(hydroxymethyl)-1,3-propanediol, A 2-methyl-2-(hydroxymethyl)-1,3-propanediol, TORIMECHI roll butane, a ****- erythritol, D-, L- and DL-threitol, adonitol, D- and L-arabitol, xylitol, dulcitol, L-iditol, D-mannitol, D-sorbitol, and racemic sorbitol are mentioned.

[0032]A polyoxyalkylene derivative is derived from the polyhydroxy compound from the above-mentioned group. It was not found out that unreacted glycerol is an effective curl inhibitor, and the unreacted pentaerythritol does not have sufficient water solubility. However, it has become clear that glycerol and the polyoxyalkylene derivative of a pentaerythritol are useful curl inhibitors. Other useful triol for oxy alkylation is trimethylolpropane, trimethylolethane, and 1,2,6-hexanetriol. As an example of some marketing of polyol / alkylene oxide condensate, Liponic^(R) EG-1, Liponic^(R) SO-20 (Lipo Chemicals Co., Paterson, NJ)-hotonol^(R) PHO-7149, Photonol PHO-7155 (Henkel.) Corporation; Ambler, PA);Voranol^(R) 230-660 and Voranol[(R)]234-630(Dow Chemical Co.,Midland, MI); Fomrez^(R) T-279, Fomrez^(R) T-315, Fomrez^(R) ET-190. And Fomrez^(R) ET-250 (Witco Corporation, Organics Division;New York, NY) is mentioned.

[0033](c) An aldose, ketose, aldonic acid, a soluble metal aldonic acid salt, and its polyalkoxy alkylene derivative constitute the curl inhibitor of a kind (c). As an example of these compounds, the erythrose of D- and L-mold, a threose, The corresponding aldonic acid of arabinose, a ribose, lixose, xylose, glucose, mannose, altrose, allose, a talose, galactose, idose, growth, and the above is mentioned. The latter examples are D-gluconic acid, D-mannonic acid, D-altronic acid, and D-Aaron acid. The example of a soluble metal aldonic acid salt is potassium gluconate.

[0034](d) Pyranosides and those polyalkoxy alkylene derivatives constitute the next kind for using for this invention of curl inhibitor. As the example, methyl alpha D-glucoside and methyl beta D-AROSHIDO is mentioned. As a polyoxyalkylene derivative, available Glucam R products are mentioned from Amerchol and Edison NJ.

[0035](e) The curl inhibitor contained in a kind (e) is a poly (alkoxy ethylene) compound which has

the above-mentioned structural formula. As this kind of a typical compound, triethylene glycol, tetraethylene glycol, Pentaethylene glycol, hexaethylene glycol, octaethylene glycol, the polyethylene glycol 200, the polyethylene glycol 400, and polyethylene-glycol 1000 grade are mentioned. A diethylene glycol is not an effective curl inhibitor. The compound of a higher molecular weight may give superfluous viscosity to ink, may cause condensation of a pigment dispersion object, and is an almost ineffective curl inhibitor. Therefore, such a compound is not preferred.

[0036](f) The curl inhibitor of the last kind contains polyoxyalkylene derivatives, such as the polyoxyalkylene derivative of aliphatic polyamine, for example, ethylenediamine, diethylenetriamine, and TORIECHI rente truck amine. As an example of marketing of the polyalkylene derivative of TORIECHI rente truck amine, it is FomrezR K-22-66 (Witco Corporation, Organics Division; New York, NY). An amine group may be neutralized all or in part by mineral acid, for example, chloride.

[0037]The mixture of the compound contained in within the limits of the above-mentioned kind and it is also useful to this invention. Especially the mixture of the compound which exists from the kind (a) or (b), and the compound which exists from a kind (e) is preferred, and 10 to 90% of one of the compounds selected in this case exists in 25 to 75% of quantity preferably on the basis of the gross weight of a curl prevention mixture. Kind (a) Although the polyoxyalkylene derivative of the compound of - (f) is prepared from ethylene, propylene oxide, or the combination of both oxide, the mixture of ethylene oxide or ethylene oxide, and propylene oxide is preferred. The reaction with single alkylene oxide may produce the mixture of the compound which has oxy alkylation of various grades on each hydroxyl group. Therefore, the above-mentioned structural formula is based on the average composition thing containing the oxyalkylene unit of a certain range. It may be random in propylene and ethylene oxide, and a block copolymer chain may be used. For example, a polyhydroxy compound is made to react to propylene oxide first, and, subsequently it is made to end by ethylene oxide one by one.

[0038]In many cases, various hydroxyl groups or those alkoxide salts are in a nonequivalence position. Therefore, they can react to alkylene oxide at a different rate by a steric factor and nucleophilicity. Therefore, various hydroxyl groups in the same compound may have a different polymerization grade. When removing paper curl substantially, in order to be effective, the curl inhibitor must exist in at least 10% of the weight of quantity on the basis of the gross weight of an ink composition. The permissible range of a curl inhibitor is 15 to 30% most preferably 12 to 55% 10 to 75% on the basis of the gross weight of ink.

[0039]Other ingredient this ink may contain other ingredients. For example, surface tension is changed using the above-mentioned surface-active agent, and osmosis can be made into the minimum. However, since the surface-active agent can make a pigment dispersion object unstable, it needs to be careful of it to secure the compatibility of a surface-active agent and other ink components. In a water-based ink, 0.01 to 5% of a surface-active agent exists in 0.2 to 3% of quantity preferably on the basis of the gross weight of ink. In order to prevent growth of a microorganism, a biocide can be used into an ink composition. As an example of such a biocide, Dowicides^(R) (Dow Chemical, Midland, MI), Nuosept^(R) (Huls America, Inc., Piscataway, NJ), OmidinesR (Olin Corp., Cheshire, CT), Nopcocides^(R) (Henkel Corp., Ambler, PA) and Troysans^(R) (TroyChemical Corp., Newark, NJ) and sodium benzoate are mentioned.

[0040]In order to remove the adverse action of heavy metal impurities, a sequestering agent like EDTA may be made to contain. The acrylic of other publicly known additive agents, for example, a viscosity controlling agent, and others or non-acrylic polymer may be added, and the various

characteristics of an ink composition may be improved. As mentioned above, many curl inhibitors of this invention are effective moisturizers for many ink-jet-ink formula things.

[0041]The ink composition of ink preparation this invention is prepared by the same method as other ink jet compositions. When using a pigment dispersion object as colorant, a dispersing element carries out preliminary mixing and prepares the underwater selected paints and dispersing agent. A dispersing process as indicated to U.S. Pat. No. 5,026,427 in level minimill, a ball mill, and ATORITTA, Or it lets a mixture pass with the fluid pressure of at least 1000 psi for two or more nozzles of the liquid jet interaction interior of a room, and can attain by producing homogeneous distribution of the paints particles in an aqueous carrier medium. Other auxiliary solvents which can improve osmosis or the DEKYAPPU (decap) characteristic may be made to exist in a dispersing process.

[0042]When using a color as colorant, a dispersing agent does not exist but there is no necessity for paints solution condensation. Color system ink is prepared with the container enough stirred rather than the dispersion device. Generally it is desirable to make the ink jet ink of a concentration gestalt, and this is taken as suitable concentration to dilute with a fluid suitable after that and use by an ink-jet-ink print system. Dilution adjusts ink to desirable viscosity, a color, hue, chroma saturation, concentration, and print region covering to a specific use.

[0043]Ink-characteristics jet speed, the separation length of a glob, dropping size, and flow stability are dramatically influenced by the surface tension and viscosity of ink. ink jet ink suitable for using it by an ink jet printing system -- 20 ** -- about 18dyne/cm- it is necessary to have the surface tension of the range of 20 dyne/cm - about 50 dyne/cm still more preferably about 70 dyne/cm 20 or less cp of viscosity which can be permitted are the ranges of about 1.0 cp - about 10.0 cp preferably at 20 ** by the suitable rheology about image setting and heat ink jet combustion supplement frequency.

[0044]Ink has the shape and the size of the drive frequency of the pressure element for the driver voltage for the physical characteristic which can suit wide range projection conditions, i.e., a heat ink jet printing device, and pulse width, a drops device on demand, or an interlocking device, and a nozzle. They suit using it with continuation, piezo-electric drops on demand and heat, or various ink jet printers like bubble jet drops on demand, and using it especially with a heat ink jet printer. Ink has the outstanding prolonged preservation stability and is not got blocked in an ink jet device. The ink of this invention is useful, especially although it uses when printing a regular paper element, but it is suitable also for using for various print media, for example, textiles, a transparent thing, etc. The printed ink image has a clear color tone, and is high-density. Ink is the component parts and compatibility of an ink jet printing device, and they are no odor intrinsically.

[0045]As mentioned above, it was found out that the ink composition of this invention provides a surprising thing with an additional advantage. For example, the ink set containing the cyanogen, the magenta, and the yellow dye system ink composition of this invention usually produces a remarkable improvement of a paper color region as compared with the color system ink which has the same dye concentration and does not contain a curl inhibitor. This color-gamut increase makes primary and secondary color clearer, and lessens the deviation of the whole paper. If the dye concentration in such ink is adjusted, a color gamut can be improved further, and a more nearly symmetrical color space is obtained. The ink jet ink set which has the above-mentioned special feature, The magenta ink containing the cyan ink containing 1.75 to 2.5% of acid blue 9 color, the yellow ink containing 1.75 to 3% of acid yellow 23, 1 to 3% of reactive red 180, and 0.3 to 1.5% of acid red 52 is included.

[0046]Another wonderful advantages of the ink of this invention are those improvement paddling characteristics. It is publicly known from USSN 07 / 845,332 (April 28, 1992 application) (the disclosure is included in this specification with a reference) to add anionic polymer in negative ion

nature color content ink, and to provide improvement of the paddling characteristic. It was found out that the same improvement in paddling is obtained using the ink of this invention which has significant more low polymer concentration (for example, comparing with polymer about 1.0% about 0.25% polymer). If polymer concentration is reduced, decap performance will become good, and generation pliability will become larger, and cost will be reduced.

[0047]

[Example]The following examples explain this invention further. Unless it writes, weight shows a part and especially percent. All the ingredients used into the ink formula thing came to hand from Aldrich Chemical, Milwaukee, and WI, unless it mentioned specially.

[0048]Operation A: Butyl methacrylate// methacrylic acid (BMA//MAA=10//10) AB block polymer (molecular weight 2400)

It is a mechanical agitation machine, a thermometer, and N2 to 12 liter flasks. It equipped with the entrance, the drying tube exit, and the addition funnel. 3750g of tetrahydrofurans ("THF") and 7.4 g of p-xylene were put into the flask. Next, the tetrabutylammonium m-chlorobenzoate catalyst (3.0 ml of 1.0M solutions which dissolved in acetonitrile) was added. 291.1 g (1.25M) of initiator 1,1-bis(trimethylsiloxy)-2-methylpropenes were poured in. The feeding I [3.0 ml of 1.0M solutions which dissolved in a tetrabutylammonium m-chlorobenzoate and acetonitrile] was started in 0 minute, and it added for 150 minutes. The feeding II [1976g (12.5M) of trimethylsilyl methacrylate] was started in 0 minute, and it added for 35 minutes. It completed after the feeding II in 180 minutes (not less than 99% of monomers reacted). The feeding III [1772g (12.5M) of butyl methacrylate] was started, and it added for 30 minutes. [0049]As of 400 minutes, the dry methanol 780g was added in the above-mentioned solution, and distillation was started. The 1300.0 g substance which has the boiling point below 55 ** all over the first step of distillation was removed from the flask. The amount of theories of the methoxy trimethylsilane (boiling point = 54 **) removed was 1144.0 g. Although distillation was continued among the secondary stage, the boiling point went up at 76 ** in the meantime. 5100 g of i-propanol was added during distillation of a secondary stage. 8007g of solvents removed all. By this operation, AB block polymer solution of 52.5%BMA//MMA which dissolved in THF and i-propanol was produced, and the paints concentrate was prepared as follows using this. It neutralized by 45.6%KOH3.86g which mixed the above-mentioned solution 19.05g with 77.1 g of deionized water, and the polymer solution was made 10%. This solution was used for Examples 13, 18, 27, and 28.

[0050]Operation B: Butyl methacrylate// butyl methacrylate is methacrylic acid (BMA//BMA//MAA=10//5/10) AB block polymers (molecular weight 3100).

Three liter flasks were equipped with a mechanical agitation machine, the thermometer, N2 entrance, the drying tube exit, and the addition funnel. 780g of tetrahydrofurans (THF) and 3.6 g of p-xylene were put into the flask. Next, catalyst tetrabutylammonium m2ml was added. 72.0 g (0.62M) of initiator 1,1-bis(trimethylsiloxy)-2-methylpropenes were poured in. The feeding I [3.2 ml of 1.0M solutions which dissolved in a tetrabutylammonium m-chlorobenzoate and acetonitrile] was started, and it added for 130 minutes. The feeding II [n-butyl methacrylate, 220g (1.55M), and 490g (3.1M) of trimethylsilyl methacrylate] was started in 0.0 minute, and it added for 40 minutes. 30 minutes after the feeding II was completed, the feeding (not less than 99% of monomers reacted) [440g (3.1M) of n-butyl methacrylate] III was started, and it added for 30 minutes.

[0051]As of 240 minutes, the dry methanol 216g was added in the above-mentioned solution, and distillation was started. The substance 210.0g which has the boiling point below 55 ** all over the first

step of distillation was removed from the flask. Although distillation was continued among the secondary stage, the boiling point went up at 76 °C in the meantime. Distillation was continued until it added 900 g of i-propanol and all were removed during distillation of a secondary stage as for 1438g of solvents. Thereby, BMA/BMA/MAA=10/5 / 10 polymer arose by the solid 57.7%. It neutralized by 45.6%KOH4.63g which mixed the above-mentioned solution 17.33g with 78.0 g of deionized water, and the polymer stock solution was made 10%. This solution was used for Example 17.

[0052]Examples 1-25 -- in the example of these, it mixed together and all color system ink prepared all the ink components or the aqueous stock solution of those until the homogeneous solution was obtained. It added stirring the water of an initial complement in this solution, and the whole quantity of ink was 100 g. The color came to hand from the commercial maker. Refining colors were used. All paints system ink (examples 19-23) 46.1 g of diethylene glycols, It prepared from the distributed concentrate containing 632 g of deionized water, 150g of FW18 carbon black pigments (DeGussa Corp., Allendale, NJ), and the 52.5% polymer solution 142.9g from the operation A, and neutralized by KOH29.0g 45.6%.

[0053]The size of the resistor put into the heat ink jet pen which has a 30-40-micron orifice at 42-50 microns, and examined ink. In order to reduce the length of time required to dry a print, the pen was finished into the ink jet printer which uses heat. The mechanical curl reduction device was not used. In order to simulate a bad example, all the pages of the double density blackout (double density blackout) which has a 1/4-inch margin were printed using various regular papers (shown below). The print face was turned up, the printed paper was placed on the flat surface, and the curl amount was become final and conclusive by measuring the distance between the edge of paper, and a flat surface at intervals of 1 hour, 24 hours, 48 hours, 72 hours, and 96 hours. The quantity which curl can permit was defined as being less than 40 mm based on aesthetics, readability, and the ease of handling.

[0054]Example 1-contrast diethylene-glycol monobutyl ether 8.0g acid blue 9 and CAS#3844-45-9 2.2g biocide 0.3g deionized water 89.5g [0055]Example 2 diethylene-glycol monobutyl ether 8.0g 2-ethyl-2-(hydroxymethyl)-1,3-propanediol 15.0g acid blue 9 2.2g biocide 0.3g deionized water 74.5g [0056]Example 3-contrast diethylene glycol 10.0g diethylene-glycol monobutyl ether 4.0gSilwet^{R} L-77 (Union Carbide Corp) 0.2g acid blue 9 2.2g deionized water 83.6g [0057]Example 4-contrast 3,3-dimethyl- 1,2-butanediol 10.0g diethylene-glycol monobutyl ether 4.0gSilwet^{R} L-770.2g acid blue 9 2.2g deionized water 83.6g [0058]Example 5 2-ethyl-2-hydroxymethyl-1,3-propanediol 10.0g diethylene-glycol monobutyl ether 4.0gSilwet^{R} L-77 0.2g acid blue 9 2.2g deionized water 83.6g [0059]Example 6 triethylene glycol 10.0g diethylene-glycol monobutyl ether 4.0gSilwet^{R} L-77 0.2g acid blue 9 2.2g deionized water 83.6g [0060]Example 7 tetraethylene glycol 10.0g diethylene-glycol monobutyl ether 4.0gSilwet^{R} L-77 0.2g acid blue 9 2.2g deionized water 83.6g [0061]Example Eight polyethylene-glycols MW400 10.0g diethylene-glycol monobutyl ether 4.0gSilwet^{R} L-77 0.2g acid blue 9 2.2g deionized water 83.6g [0062]Example 9 sorbitol 10.0g diethylene-glycol monobutyl ether 4.0gSilwet^{R} L-77 0.2g acid blue 9 2.2g deionized water 83.6g [0063]Example 10 tris (hydroxymethyl) aminomethane 10.0g diethylene-glycol monobutyl ether 4.0gSilwet^{R} L-77 0.2g acid blue 9 2.2g deionized water 83.6g [0064]Example 11 neopentyl glycol 7.5g tetraethylene glycol 7.5g diethylene-glycol monobutyl ether 4.0gSilwet^{R} L-77 0.2g acid blue 9 2.2g deionized water 78.6g [0065]Example 12 2-methyl-2-(hydroxymethyl)-1,3-propanediol 7.5g tetraethylene glycol 7.5g diethylene-glycol monobutyl ether 4.0gSilwet^{R} L-77 The 0.2g acid blue 9. 2.2g deionized water 78.6g [0066]Example 13 2-methyl-2-propyl-1,3-propanediol 7.5g tetraethylene glycol 7.5g diethylene-glycol monobutyl ether 4.0gSilwet^{R} L-77 0.2g acid blue 9 2.2g deionized water 78.6g [0067]

Example 142,2-diethyl- 1,3-propanediol 7.5g tetraethylene glycol 7.5g diethylene-glycol monobutyl ether 4.0gSilwet^{R} L-77 0.2g acid blue 9 2.2g deionized water 78.6g [0068]Example 152-ethyl-2-(hydroxymethyl)-1,3-propanediol 7.5g tetraethylene glycol 7.5g diethylene-glycol monobutyl ether The 4.0gSilwet^{R} L-770.2g acid blue 9. 2.2g deionized water 78.6g [0069]Example 162-ethyl-2-(hydroxymethyl)-1,3-propanediol 18.0g dipropylene glycol 2.0gSilwet^{R} L-7607 Block polymer from the 0.5g operation A The 2.5g acid blue 9. 2.2g biocide 0.3g deionized water 74.5g [0070]Example 173-methyl- 1 and 3 and 5-pentanetriol (Fluka Chemical) 16.0gSilwet^{R} L-7607 Block polymer from the 0.8g operation B 4.0g acid blue 9 2.2g biocide 0.3g deionized water 76.7g[0071]example 182-ethyl-2-hydroxymethyl-1,3-propanediol The 4.0g3-methyl- 1 and 3 and 5-pentanetriol 12.0gSilwet^{R} L-7607 Block polymer from the 0.8g operation A . 4.0g acid blue 9 2.2g biocide 0.3g deionized water 76.7g [0072]Example 19-contrast diethylene glycol 26.7g of 18.7g pigment dispersion object concentrates deionized water 55.8g [0073]Example 202-ethyl-2-(hydroxymethyl)-1,3-propanediol 17.5g pigment dispersion object concentrate 26.7g deionized water 55.8g example 21 alpha D-glucose 26.7g of 17.5g pigment dispersion object concentrates deionized water 55.8g [0074]Example 22 methyl-alpha D-glucoside 26.7g of 17.5g pigment dispersion object concentrates deionized water 55.8g example 23 D-gluconic acid Potassium salt 17.5g pigment dispersion object concentrate 26.7g deionized water 55.8g [0075]Example 24 tris(hydroxymethyl) aminomethane 20.0gSilwet^{R} L-7607 1.0g acid blue 9 2.2g biocide 0.3g deionized water 76.5g [0076]Example 25 tris(hydroxymethyl) aminomethane HCl 12.0g tris(hydroxymethyl) aminomethane The 3.0gAerosol^{R} OT (Fisher Scientific) 0.3g acid blue 9. 2.2g biocide 0.3g deionized water 82.2g [0077]

[Table 1]

表 1

実施例	温度/RH ³	用紙	紙のカール (mm)				
			1時間	24時間	48時間	72時間	96時間
1 (対照)	周囲温度	GB ¹	>90° ⁴				
		SH ²	>90°				
2	周囲温度	GB	20	5			
		SH	30	17			
3 (対照)	周囲温度	GB	31	60			
		SH	44	100			
4 (対照)	周囲温度	GB	>90°			管	
		SH	>90°			管	
5	周囲温度	GB	18			8	
		SH	37			35	
6	周囲温度	SH	15			50	
7	周囲温度	SH	20			30	

7	周囲温度	SH	20		30
8	周囲温度	SH	50		35
9	周囲温度	GB	27		14
		SH	44		33
1 0	周囲温度	GB	19		14
		SH	34		24
1 1	周囲温度	GB	14	17	15
		SH	16	35	35
1 2	周囲温度	GB	7	4	3
		SH	6	3	4
1 3	周囲温度	GB	14	28	41
		SH	10	30	26
1 4	周囲温度	GB	17	26	29
		SH	15	22	26
1 5	周囲温度	GB	4	3	2
		SH	6	3	2

[0078]

[Table 2]

表 1 (続き)

実施例	温度/RH ³	用紙	紙のカール (mm)				
			1時間	24時間	48時間	72時間	96時間
1 6	周囲温度	GB	13	3			
		SH	18	8			
1 6	15°C/20%	GB	37	30			
		SH	20	18			
1 7	15°C/20%	GB	37				
		SH	25				
1 8	15°C/20%	GB	28		19		
		SH	16		10		
1 9 (対照)	周囲温度	GB	3	66	管		

1 9 (対照)	周囲温度	GB	3	66	管
		SH	3	管	管
2 0	周囲温度	GB	16	6	5
		SH	13	6	6
2 1	周囲温度	GB	11	7	5
		SH	26	14	10
2 2	周囲温度	GB	19	30	31
		SH	20	32	35
2 3	周囲温度	GB	24	18	14
		SH	24	16	13
2 4	15°C/20%	GB	13		
		SH	17		
2 5	周囲温度	GB	8	1	
		SH	9	4	

注：1. GB=Gilbert^(R) ボンド紙 (25%綿)、形式1057 (Mead Company, Dayton, Ohio)

2. SH=Springhill Relay DP (International Paper, Tuxedo, NY)

3. 印刷及び保存の条件

4. >90°は“U”字形に上方及び下方にカールした縁を意味する。

[0079]Example The cyanogen which has a constituent of 26 following, magenta, and yellow ink were prepared.

cyanogen diethylene-glycol monobutyl ether . 7.0gSilwet^{R} L-7607. 1.0g acid blue 9 2.25g biocide . 0.3g deionized water . 89.45g magenta diethylene-glycol monobutyl ether 7.0gSilwet^{R} L-7607 1.0g acid red 52 and CAS#3520-42-1 0.6g reactive red 180 and CAS#85586-40-9. 2.75g biocide 0.3g deionized water 88.35g yellow diethylene-glycol monobutyl ether 7.0gSilwet^{R} L-7607 1.0g acid yellow 23 and CAS#1934-21-0 2.5g biocide 0.3g deionized water 89.2g [0080]Ink was printed on the regular paper indicated to Table 2 by the same method as Examples 1-25. Curl is measured like the above about cyan ink, and it reports to Table 2. Color space data was obtained by Hunterlab PICCS 4800 (Hunter Associate Labs, Inc., Reston, VA) using the light source and 2 observation device. A result is shown in the following table 3.

[0081]Example The same operation as Example 26 was performed using the cyanogen which has a constituent of 27 following, magenta, and yellow ink.

Cyanogen 2-ethyl-2-(hydroxymethyl)-1,3-propanediol 18.0g dipropylene glycol 2.0gSilwet^{R} L-7607

Block polymer from the 0.5g operation A The 2.5g acid blue 9. 2.25g biocide 0.3g deionized water . 74.45g magenta 2-ethyl-2-(hydroxymethyl)-1,3-propanediol 18.0g dipropylene glycol 2.0gSilwet^{R} L-7607 Block polymer from the 0.5g operation A The 2.5g acid red 52. 0.6g reactive red 180 2.75g biocide . 0.3g deionized water 73.35g yellow 2-ethyl-2-(hydroxymethyl)-1,3-propanediol 18.0g dipropylene glycol 2.0gSilwet^{R} L-7607 Block polymer from the 0.5g operation A . 2.5g acid yellow 23 2.5g biocide 0.3g deionized water 74.2g [0082]Example The same operation as Example 26 was performed using the cyanogen which has a constituent of 28 following, magenta, and yellow ink. Cyanogen 2-ethyl-2-(hydroxymethyl)-1,3-propanediol 18.0g dipropylene glycol 2.0gSilwet^{R} L-7607 Block polymer from the 0.5g operation A The 2.5g acid blue 9. 2.0g biocide 74.7g of 0.3g deionized water magenta 2-ethyl-2-(hydroxymethyl)-1,3-propanediol 18.0g dipropylene glycol 2.0gSilwet^{R} L-7607 Block polymer from the 0.5g operation A . 2.5g acid red 52 1.0g reactive red 180 1.6g biocide 0.3g deionized water 74.1g yellow 2-ethyl-2-(hydroxymethyl)-1,3-propanediol 18.0g dipropylene glycol . 2.0gSilwet^{R} L-7607 Block polymer from the 0.5g operation A 2.5g acid yellow 23 2.75g biocide 0.3g deionized water 73.95g [0083]
[Table 3]

表 2

実施例	温度/RH ³	用紙	紙のカール (mm)				
			1時間	24時間	48時間	72時間	96時間
2 6 (対照)	周囲温度	GB ¹	管	管			
		SH ²	管	管			
2 7	15°C/20%	GB	37	30			
		SH	20	18			

注 1、2 および 3 は表 1 参照

[0084]

[Table 4]

表 3

実施例	用 紙	色	色 相	明 度	彩 度	色 域
2 6	GB ¹	赤	5.57 R	5.12	12.34	775
		緑	3.52 G	5.16	9.97	
		青	8.23 PB	3.14	9.81	
		シアン	8.19 B	5.80	11.57	
		マゼンタ	3.59 RP	5.27	14.77	
	SH ²	黄	6.72 Y	9.13	11.42	729
		赤	5.89 R	5.12	11.71	
		緑	3.38 G	5.15	9.79	
		青	8.04 PB	3.46	9.21	
		シアン	7.68 B	5.68	11.21	
		マゼンタ	3.88 RP	5.26	13.97	
		黄	6.95 Y	9.05	11.03	

[0085]

[Table 5]

表 3 (続き)

実施例	用 紙	色	色 相	明 度	彩 度	色 域
2 6	HAM ³	赤	5.89 R	5.13	11.40	683
		緑	3.16 G	5.22	9.48	
		青	8.17 PB	3.56	9.01	
		シアン	8.01 B	5.72	10.92	
		マゼンタ	3.68 RP	5.32	13.63	
		黄	6.36 Y	8.94	10.89	
2 7	GB	赤	5.94 R	5.01	14.11	918
		緑	2.45 G	5.14	11.54	
		青	8.95 PB	2.88	10.03	
		シアン	7.88 B	5.64	12.16	
		マゼンタ	4.75 RP	5.02	15.59	
		黄	7.51 Y	9.13	12.08	
	SH	赤	6.29 R	4.94	14.48	939
		緑	2.17 G	5.10	11.79	
		青	9.11 PB	2.69	10.04	
		シアン	7.70 B	5.55	11.98	
		マゼンタ	4.92 RP	4.95	15.68	
		黄	7.34 Y	9.17	12.43	
	HAM	赤	6.30 R	4.93	14.06	905
		緑	2.23 G	5.02	11.41	
		青	8.98 PB	2.90	9.80	
		シアン	7.51 B	5.62	11.94	
		マゼンタ	4.93 RP	4.94	15.31	
		黄	7.17 Y	9.10	12.27	

[0086]

[Table 6]

表 3 (続き)

実施例	用 紙	色	色 相	明 度	彩 度	色 域
2 8	GB	赤	6.26 R	4.83	14.06	997
		緑	1.83 G	5.18	11.96	
		青	8.47 PB	2.93	11.94	
		シアン	7.39 B	5.83	11.83	
		マゼンタ	2.88 RP	5.02	16.75	
		黄	6.81 Y	9.08	12.85	
	SH	赤	6.34 R	4.91	13.39	970
		緑	1.86 G	5.29	12.10	
		青	8.33 B	3.04	11.96	
		シアン	6.90 B	5.86	11.74	
		マゼンタ	3.08 RP	5.00	16.02	
		黄	6.88 Y	9.01	12.36	
	HAM	赤	6.47 R	4.92	13.52	939
		緑	1.68 G	5.18	11.64	
		青	8.45 PB	3.11	11.48	
		シアン	6.91 B	5.80	11.62	
		マゼンタ	3.03 RP	4.93	16.09	
		黄	6.62 Y	8.91	12.5	

注：1. GB=Gilbert^(R) ボンド紙 (25%綿)、形式1057 (Mead Company, Dayton, Ohio)

2. SH=Springhill Relay DP (International Paper, Tuxedo, NY)

3. HAM=Hammermill Fore^(R) DP (Hammerhill Papers, Erie, PA)

[0087]Although the ink of Example 27 had the same dye concentration as the ink of Example 26, the ink of Example 27 contained the curl inhibitor. Data explains the improvement (26%) with a usually significant paper color region by curl inhibitor addition. Although Example 28 was the same as Example 27 except dye concentration, it showed improvement (increase of 5%) of a color gamut, and improvement (increase of 18%) of blue chroma saturation.

[Translation done.]